

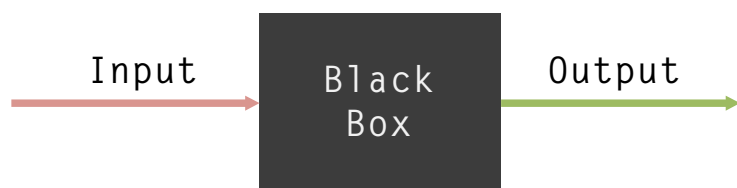
# WattsAptamer Simulation Model

A simulation model was constructed of a PBEC (photo-bioelectrochemical cell) using AnyLogic. It is to be used for illustrational purposes.

AnyLogic is a simulation modeling tool that supports multiple simulation methods such as system dynamics, discrete event and agent based modeling. AnyLogic consists of a graphical modeling language working with Java code extensions.

## “Black box” strategy

In order to reduce the complexity of the simulation model, a “black box” strategy was followed. A “black box model” requires specific information as input where after the system utilizes pre-programmed logic to return output to the user. Many “black box models” can be used which uses each other’s output. (Investopedia, 2016) Making use of a “black box model” ensured that functional areas relevant to the proposed model were isolated without neglecting variability, as a result of the influence of other parameters.



## The first “black box”

The first “black box” to be addressed relates to the influence of the material type used for the casing of the battery. Perspex and glass were considered as possibilities. Absorption properties of material influence transmitted light. This will in return affect the light reaching the attached photosystems. Perspex of 4.5 mm thick has a solar light transmittance of 37 % and visible light transmittance of 33 %. Glass has a solar transmittance of 90 % and visible light transmittance of 91 %. (Altuglas International, 2016)

A changed light intensity ( $\mu$  mole photons.m<sup>-2</sup>.s<sup>-1</sup>) is obtained as an output as seen in Figure 1 below.



Figure 1: The first “black box”

## The second “black box”

The second “black box” in the model represents the process of photosynthesis occurring in photosystems within the attached thylakoid membranes.

Photosynthetic electron transfer’s relative proton to electron stoichiometries (H<sup>+</sup>/e<sup>-</sup> ratios) was obtained from living tobacco plant leaves under steady-state illumination. Electron transfer fluxes as well as turnover rates of linear electron transfer through the cytochrome (cyt) b6f complex were estimated. (Colette A. Sacksteder, 2000) In Figure 2, fluorescence yields and electron flux of photosystem II is plotted. Yields from fluorescence during saturation pulses,  $F'_M$  (closed squares) and yields from fluorescence in the steady-state,  $F_s$  (open circles), were obtained at varying light intensities. Photosystem II and associated light-harvesting complexes’ ( $F_v/F'_M$  or  $\phi_{II}$ , open diamonds) quantum yield and an estimate of the electron flux of photosystem II ( $i \cdot \phi_{II}$ ) were calculated, as described in the above mentioned report.

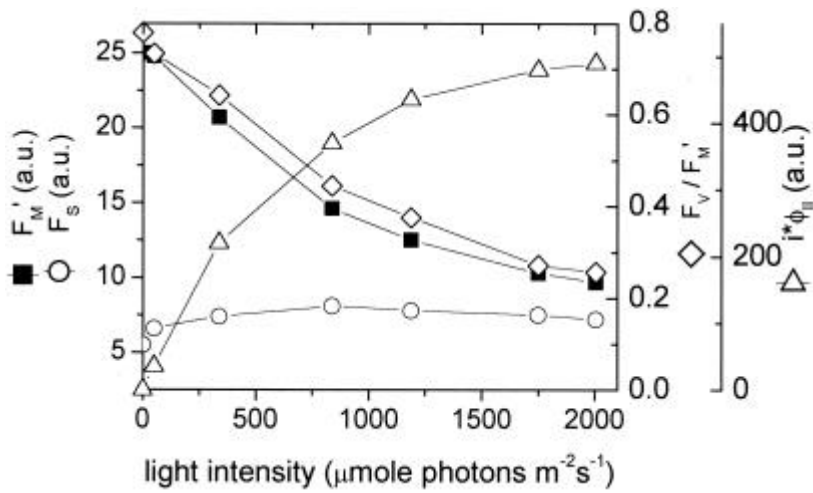


Figure 2: Photosystem II electron flux and various fluorescence yields as a function of light intensity

The estimate of electron flux ( $i \cdot \phi_{II}$ ) (open diamonds) is of importance in describing what happens in the second “black box” of this simulation model. A line of best fit was retrieved from the information in Figure 2 and transformed to a polynomial function plotted in Figure 3, described by the following equation:

$$f(x) = -2 \times 10^{-4}x^2 + 0.5938x + 13.837 \quad [1]$$

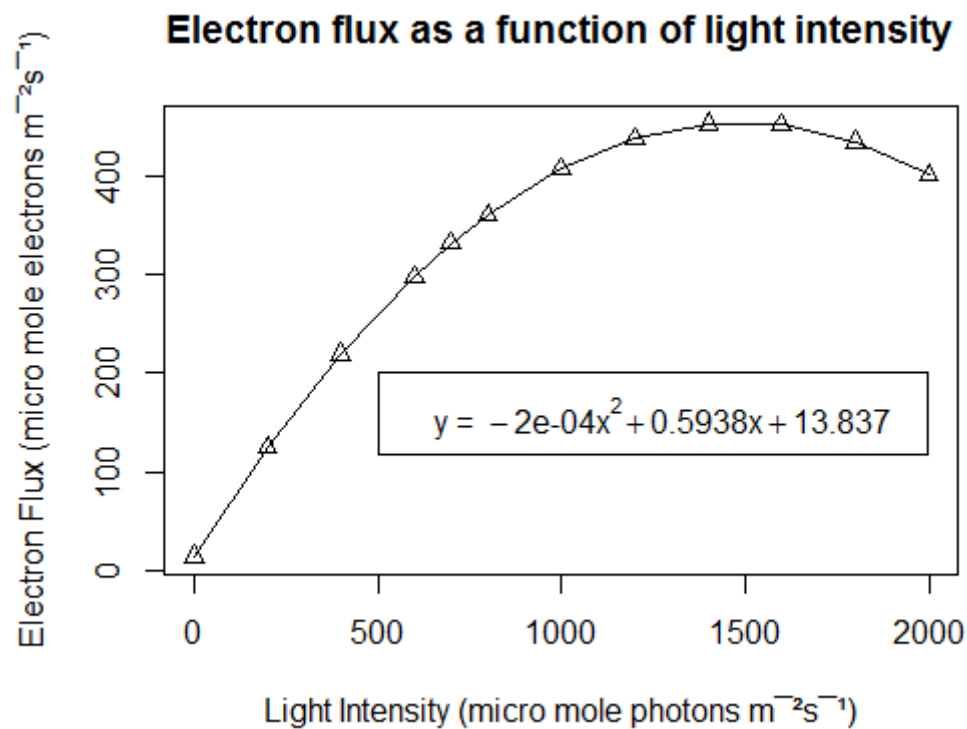


Figure 3: Electron flux of photosystem II as a function of light intensity

The above figure describes the electron flux obtained from a single photosystem II. There is a single photosystem II inside each  $7.5 \times 10^{-9}$  m thick thylakoid. (Kirschner Lab, 2001)

This was used to calculate the quantity of photosystems II possibly located on the surface area of the graphene



electrode.

Figure 4: The second "black box"

As seen in the above Figure 4, light intensity ( $\mu$  mole photons  $m^{-2}s^{-1}$ ) is used as input for the first black box, where after equation [1] describes processes happening inside the box and gives an output of electron flux ( $\mu$  mole electrons. $m^{-2}.s^{-1}$ ).

## The third "black box"

Fick's diffusion laws are used to describe the movement of electrons from the photosystems to the graphene electrode. Fick's first law is given as:

$$J = -D \frac{dc}{dx} \quad [2]$$

Where

$J$  = diffusion flux (electrons. $m^2.s^{-1}$ )

$D$  = diffusion coefficient ( $m^2.s^{-1}$ )

$c$  = concentration (electrons. $m^{-3}$ )

$x$  = distance (m)

Equation [2] can be rearranged into Equation [3]:

$$V = \frac{(P_1 - P_2) \cdot A \cdot D}{x} \quad [3]$$

Where

$V$  = amount of substance (electrons. $s^{-1}$ )

$P_1$  = concentration at point 1 (electrons. $m^{-2}.s^{-1}$ )

$P_2$  = concentration at point 2 (electrons. $m^{-2}.s^{-1}$ )

$A$  = area ( $m^2$ )

$D$  = diffusion coefficient ( $m^2.s^{-1}$ )

$x$  = distance (m)

The concentration of electrons at point 1 is the changing electron flux produced by the thylakoid membranes and obtained from the second "black box". It is assumed that the electron concentration at point 2, which is the surface area of the graphene electrode, is infinitely small. The exposed surface area ( $A$ ) of the graphene electrode is where the thylakoid membranes are attached. The distance ( $x$ ) resembles the space between the thylakoid membrane and the surface area of the graphene. Using aptamers, this distance amounts to  $24 \times 10^{-9}$  m. (Barendse, 2016) Without the use of aptamers an 50% increase in distance is assumed.

The diffusion coefficient of electrons in solution is calculated using Einstein's relation, also known as Einstein–Smoluchowski relation:

$$D = \mu k_B T \quad [4]$$

Where

$D$  = diffusion coefficient ( $m^2.s^{-1}$ )

$\mu$  = mobility or ratio of particle's terminal drift velocity to an applied force

$k_B$  = Boltzmann's constant ( $J.K^{-1}$ )

$T$  = Absolute temperature (K)

Boltzmann's constant of  $1.3806 \times 10^{-23} J.K^{-1}$  is used. An absolute temperature of 273.16 K is assumed as the battery will be operating at room temperature. The electric mobility in water of  $20 \times 10^{-8} m.^2V^{-1}.s^{-1}$  is used. The diffusion coefficient  $m^2s^{-1}$  is calculated as  $2.069 \times 10^{-27} m^2.s^{-1}$

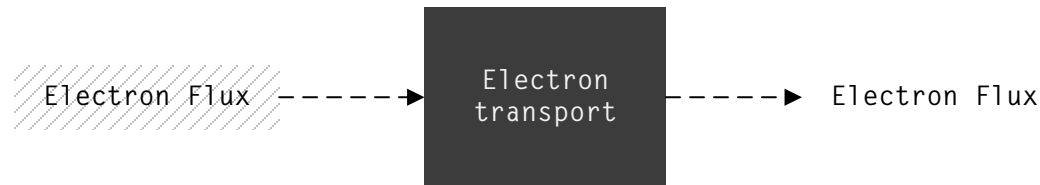


Figure 5: The third "black box"

In the above Figure 5, electron flux ( $\mu$  mole electrons. $m^{-2}.s^{-1}$ ) is used as input for the second black box, where after equation [3] and [4] describe the diffusion of electrons from the thylakoid membranes to the graphene electrode. An output of a number of electrons per second is obtained.

## The Overall Model Logic

Combining all of the "black boxes" results in the model logic as illustrated in Figure 6. Changeable parameters include: light intensity ( $\mu$  mole photons. $m^{-2}.s^{-1}$ ), casing material (Perspex or glass), electrode size and whether or not to select thylakoid attachment by making use of aptamers. The main measurable is current (A).

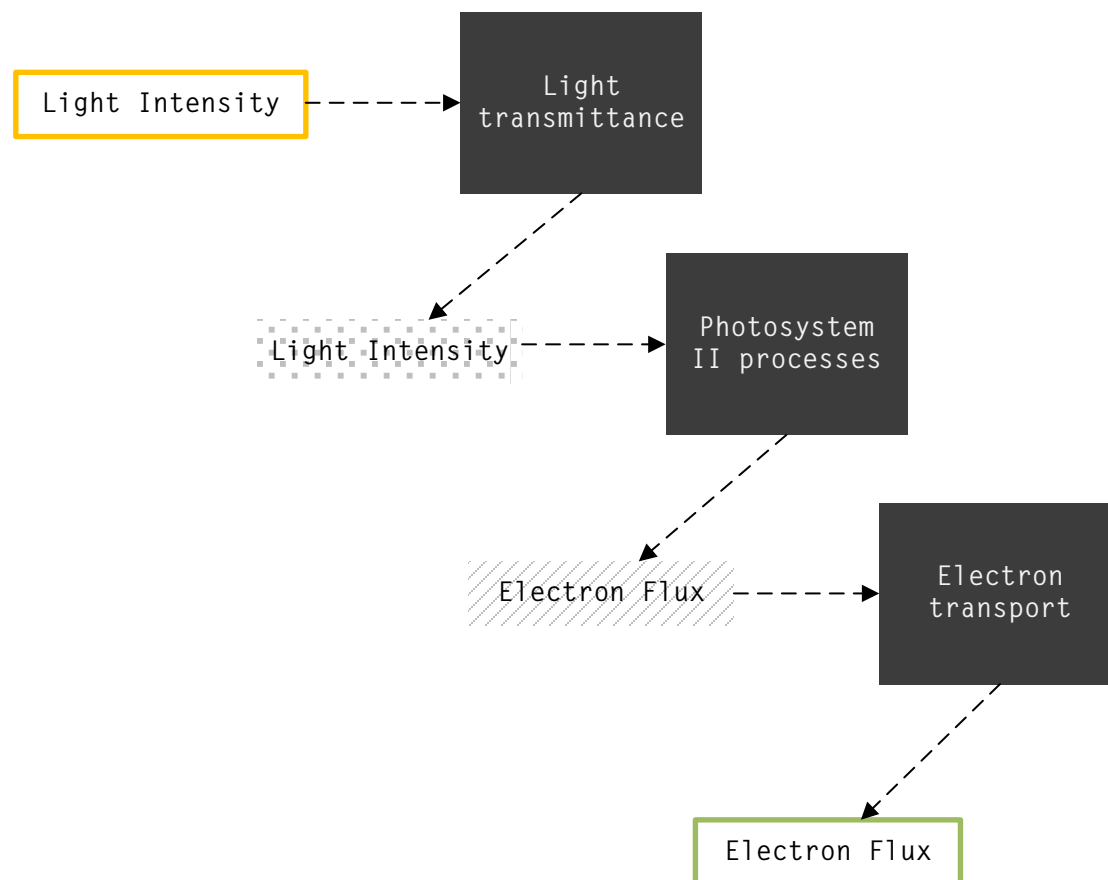


Figure 6: The combination of "black boxes" used in the model

## User Interface and Animation

Buttons and sliders are added to allow the user to change specific parameters. Graphs of both the current (A) measured and the influence of light intensity on the electron flux produced are drawn dynamically. A 3D illustration of the PBEC is also presented which is animated as the user changes parameters.

## Model Results

After multiple runs, the highest yield resulting in a current of  $5.342 \times 10^{-21} \text{A}$  was obtained with the following parameter settings: Light intensity of  $1840 \mu \text{mole photons.m}^{-2}.\text{s}^{-1}$ ; using glass as casing material; keeping the electrode surface area at  $3.2 \text{ cm}^2$ ; making use of aptamers to attach thylakoids to the electrode.